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DEVELOP SPUTTER DEPOSITED, GRADED METAL-ZR02 COATING TECHNOLOGY--ETC(U)  
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## Periodic Technical Report

### Develop Sputter Deposited, Graded Metal-ZrO<sub>2</sub> Coating Technology for Application to Turbine Hot Section Components

R. Busch

October 11, 1976

Report Period: November 21, 1975  
to September 30, 1976

Prepared Under Contract  
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REPORT PERIOD: November 21, 1975  
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UNCLASSIFIED ABSTRACT

The deposition of ceramic coatings on gas turbine hot section components by high-rate sputtering was investigated. Stabilized zirconia was the primary ceramic used, however some work was done with magnesium zirconate. The main thrust of the program was the development of methods to improve coating adherence by accommodation of the strain due to the expansivity difference between zirconia and the superalloy components. The use of a graded composition interlayer was the only method which proved useful; its utility was found to depend on the ductility of the metallic constituent and the details of the composition gradient. When the coatings were evaluated by rapid thermal cycling between 25 and 950°C, graded composition layers up to 0.1 mm thick survived six complete cycles. Pure zirconia overlayers were less adherent.

A second area of investigation involved the stoichiometry of the zirconia deposits, which exhibited oxygen deficiencies dependent on deposition rate and substrate temperature. The deficiencies were reduced by oxygen additions to the sputtering atmosphere, but it was necessary to simultaneously reduce the deposition rate and substrate temperature to reach approximate stoichiometry.

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## INTRODUCTION

This report describes details of the work performed during the second or final reporting period and summarizes the results of the first reporting period. The program objective was the development of adherent zirconia coatings for gas turbine hot section components. The motivation for the program was twofold -- the coatings were expected to provide protection from hot corrosion or sulfidation; and, depending on the thickness achievable with satisfactory adherence, a useful thermal barrier effect might be obtained. This would permit reduction of metal temperature or cooling air flow requirements, or alternately could be used to permit increased turbine inlet temperatures. Accordingly, the selection of zirconia was based primarily on the basis of its low thermal conductivity.

The scheme investigated for obtaining adherence of the zirconia coatings was the use of a graded composition interlayer, ranging from pure metal at the superalloy surface to pure zirconia at the opposite edge. Deposition of this layer required a sputtering apparatus which combined direct current and radio frequency biased targets in a common discharge. Design and construction of such an apparatus, together with investigation of graded composition layers containing nickel or CoCrAlY, formed the major part of the first reporting period.

The second or final reporting period was devoted to more thorough investigation of the graded composition layers, including the properties of the metallic constituent of the layers, the composition profile and the total thickness. The influence of deposition parameters such as rate and substrate temperature also received attention.



## EXPERIMENTAL PROCEDURE

### SPUTTERING

The graded ceramic coatings were formed by high rate sputtering in the apparatus shown in Figure 1. The apparatus utilized the triode, or supported discharge, mode of operation. The metal and ceramic targets were immersed in the discharge and biased by dc and rf power supplies, respectively. The centrally located substrates were rotated at a speed which resulted in the individually deposited metal and ceramic layers being  $< 50 \text{ \AA}$  thick.

Five substrates of up to 1/2 inch diameter were coated simultaneously, e.g. pins and wedges for burner rig testing. The substrate materials were IN738, IN792, and René 80.

The metal targets were fabricated from commercial plate except Ni50Cr and CoCrAlY, which were hot pressed compacts. The ceramic targets were plasma sprayed calcia stabilized zirconia on steel backing plates.

The deposition procedure involved evacuating the apparatus to  $10^{-8}$  torr, and back filling with research grade krypton to a pressure of  $3 \times 10^{-3}$  torr, which was maintained by balancing the in-leak rate against the throttled diffusion pump. After igniting the discharge, the substrates were ion etched to provide a clean surface. The etch was divided into two or three parts to allow the maximum substrate temperature during etching to be kept under  $300^{\circ}\text{C}$ . This had previously been found necessary to prevent the formation of an undesirable surface layer.<sup>(1)</sup>

After the etch was completed, the metal target was biased to begin deposition. The metal target bias voltage was decreased with time as the ceramic target power was increased according to schedules described later. At a point where the ceramic

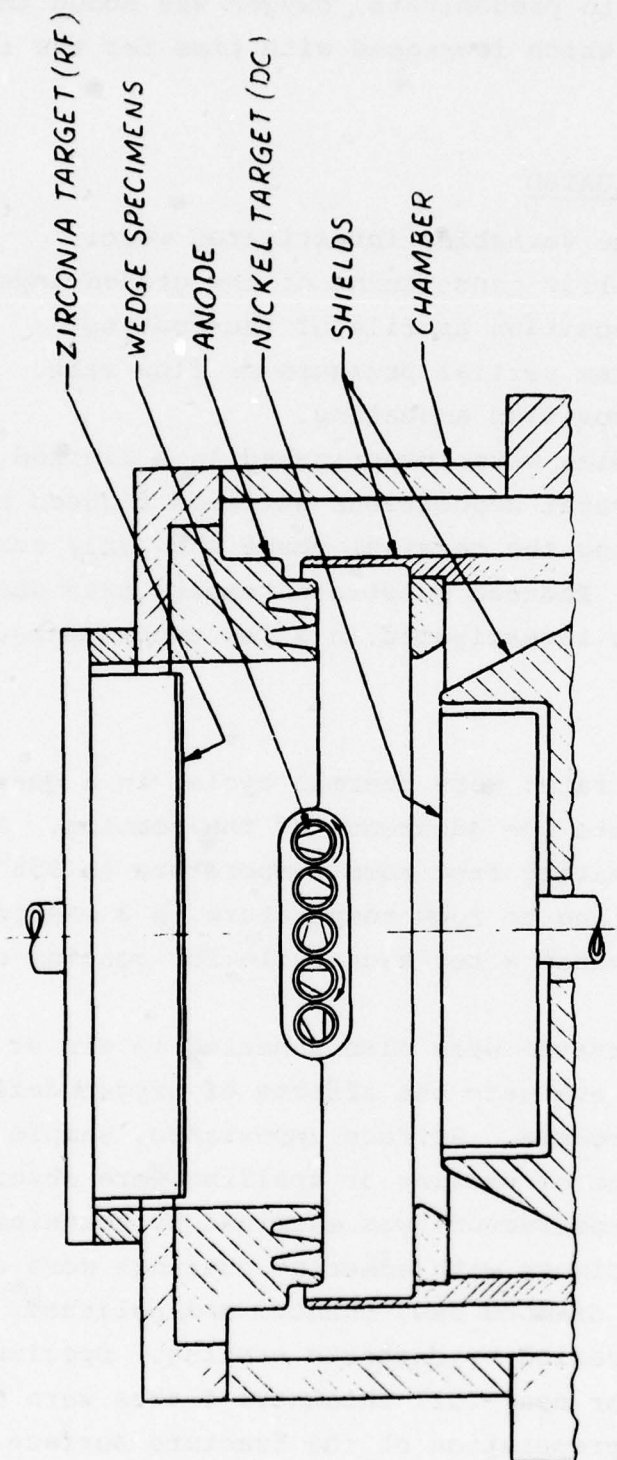


FIGURE 1. Sputter-Deposition Apparatus Used for Forming Composite Metal-Ceramic Coatings on Burner-Rig Test specimens.

sputtering began to predominate, oxygen was added to the discharge at a rate which increased with time for the remainder of the deposition.

#### VARIABLES INVESTIGATED

The principle variables investigated were:

1. The metallic constituent of the graded layer.
2. The composition profile of the coating.
3. The oxygen partial pressure or flow rate.
4. Post deposition annealing.

Other variables were investigated in a limited number of experiments. Several depositions utilized reduced power levels, particularly during the terminal phase when only ceramic was being sputtered. Reduced substrate temperatures and applied bias voltage were investigated in a few experiments.

#### EVALUATION

Coated substrates were thermal cycled in a quartz lamp furnace to evaluate the adherence of the coating. A typical cycle involved heating from room temperature to 950°C in 45 seconds, and cooling to room temperature in 3 minutes. Substrates were examined after each cycle for coating cracks and spalls.

Coated substrates were also annealed in air at 750°C for several hours to evaluate the effects of oxygen deficiency of the deposited zirconia. Surface appearance, sample weight changes and degree of crazing or spalling were observed.

Coating microstructure was examined by scanning electron microscopy. Specimens with adherent coatings were sectioned with a low speed diamond saw, mounted and polished. The structure was best revealed by cathodic etching. Specimens which spalled in full or near-full thickness flakes were examined without further preparation of the fracture surface. In both cases, the composition profile was obtained by line scan x-ray fluorescence.



## RESULTS AND DISCUSSION

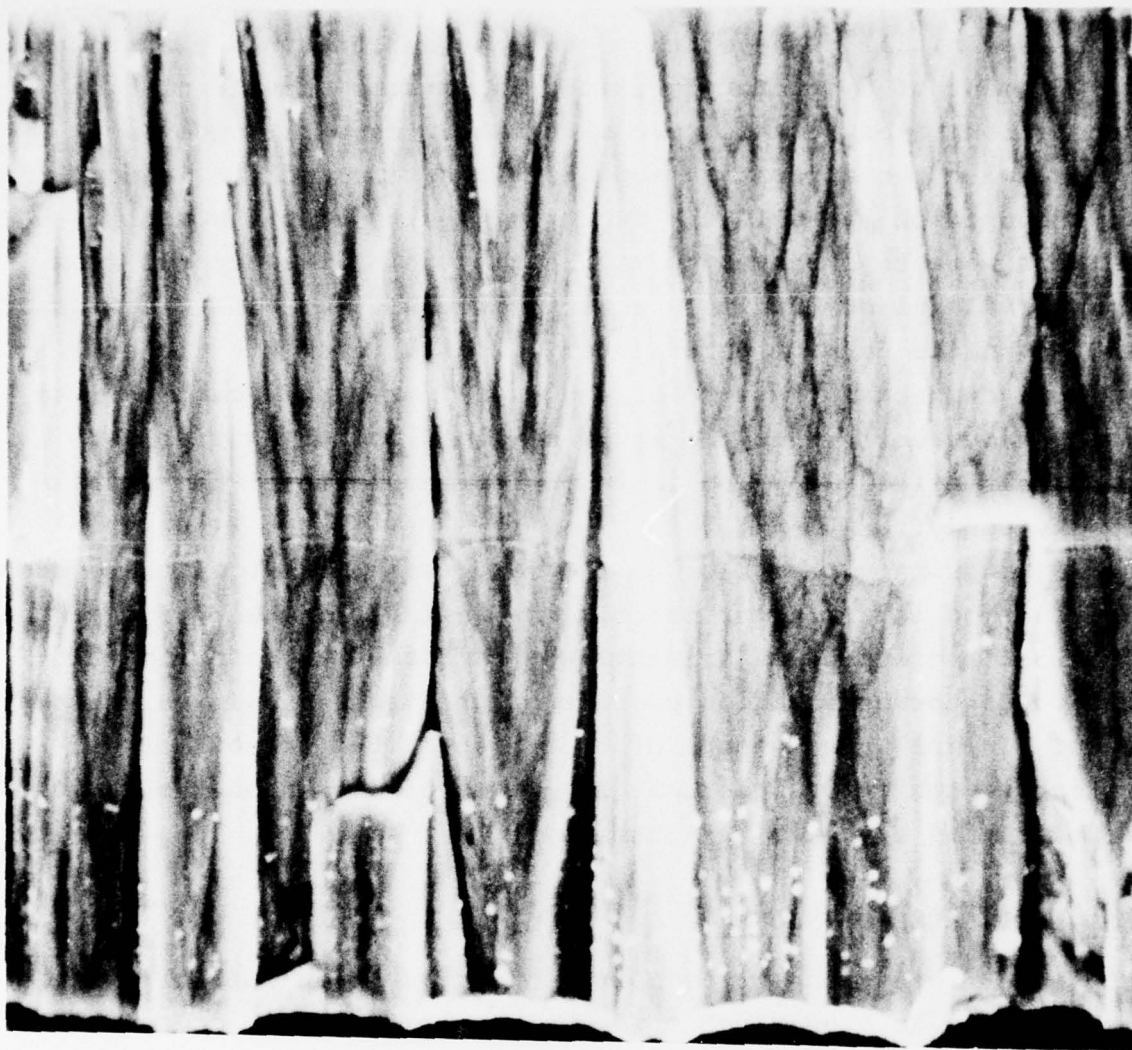
The initial phase of this program was concerned with the development of a sputter deposition apparatus capable of high deposition rates with ceramic materials. As experience was gained with the apparatus, modifications were made to improve its deposition capability. Two main results of these modifications were to improve the microstructure of the deposit from a materials viewpoint, i.e. a reduced density of growth defects, etc.; and to permit operation of the apparatus with higher effective partial pressure of oxygen. These modifications were made concurrently with the study of the principal variables, and their effects must be included in discussion of the results of the study.

The primary variable was the metal constituent of the graded composition layer. Four materials were investigated; for each material a group of experiments was performed to determine the effect of the composition profile of the graded layer on adherence. In the later groups of experiments, the effects of different partial pressures and flow rates of oxygen on the stoichiometry of the zirconia was examined.

### COATINGS BASED ON NICKEL

The first group of deposits consisted of an initial graded layer 0.002 to 0.003 inch thick which was graded in composition from nickel to zirconia, and a zirconia layer of similar thickness. The zirconia was stabilized with 5 mole percent calcia. The deposits had a relatively open microstructure, Figure 2, and were adherent through five thermal cycles. When spalling occurred, it initiated at corners of the burner rig wedge specimens and spread along edges. Generally, the spalled material consisted of the zirconia layer; most of the thickness of the graded composition layer remained bonded.





—20  $\mu\text{m}$ —

FIGURE 2. Cross-Sectional View of a Graded Nickel-Zirconia Coating Deposited in Early Work. Open Columnar Structure Parallel to Growth Direction. SEM Photograph.

Spalling occurred at the low temperature end of the cooling portion of the thermal cycle, generally below 200°C and frequently at or near room temperature. In this temperature region, the zirconia and zirconia-rich portions of the coating were in compression due to their smaller expansivity. Since the coating may be assumed to have been stress-free at the deposition temperature<sup>(2)</sup> (600-700°C), and did not fail in the first few thermal cycles, it is hypothesized that the zirconia layer grew by creep in tension during the high temperature portion of each cycle, which increased the compressive stress at the low temperature end of the cycle until failure occurred. This behavior is in contrast to that predicted by finite element calculations which indicated maximum tensile stresses far in excess of the anticipated strength of the zirconia at the maximum temperature of the cycle.<sup>(3)</sup>

Once the continuous or closed loop nature of the coating was broken by localized spalling, the areas which remained bonded were much more resistant to damage by additional thermal cycling. Islands of coating a few square centimeters in area remained bonded after several extreme cycles employing oxyacetylene torch heating and ice water quenching. The total area of these islands comprised about half of the specimen surface area. The zirconia layer in the as deposited condition yielded a poorly defined x-ray diffraction pattern. After exposure to the 950°C peak cycle temperature, the pattern definition improved, and the tetragonal crystal structure was identified. This was unexpected, since stabilized zirconia is cubic<sup>(4)</sup>, and transfer of the calcium stabilizer was verified by x-ray fluorescence. However, it did not appear to affect the coating adherence, since the zirconia transformation temperature was not exceeded, and since failure occurred at the room temperature end of the thermal cycles.

In later work with nickel, the effects of the composition profile and oxygen partial pressure on the adherence of the graded layer were studied. These coatings did not have a pure zirconia layer of appreciable thickness, e.g. mils, but did have a thin outer layer on the order of a few tenths of a mil which was substantially pure zirconia. This layer was deposited during the last stage of the variable power dc and rf sputtering, when the metal target surface became covered with an insulating film of zirconia. Since the results of this work were similar to those obtained with the nickel-chromium alloys, they will be discussed in that section of the paper.

#### COATINGS BASED ON CoCrAlY

The original concept of the graded composition layer involved only the elastic and thermal properties of the materials and did not envision the plastic deformation of the metallic constituent. Therefore, metal compositions more suitable to a sulfidation environment and substantially less plastic were substituted for the nickel. The CoCrAlY composition (Co 25 Cr 12 Al 0.5 Y) currently used as a PVD overlay coating was used in a series of experiments. The original deposits were similar in configuration to those based on nickel, i.e. comparable thicknesses of graded composition layer and pure ceramic layer. These deposits spalled the entire ceramic layer during the heating portion of the first thermal cycle. In addition, a substantial portion of the thickness of the graded composition layer spalled upon cooling from the first cycle.

In two subsequent experiments, the entire coating thickness was of graded composition, i.e. no pure zirconia layer was deposited. In one case, the grading was not carried to completion, as indicated by the electrical conductivity of the coating surface. Neither coating maintained adherence through the



second thermal cycle, although the incompletely graded specimens suffered somewhat less coating loss.

In contrast to the results with nickel, where most of the graded layer thickness remained bonded to the superalloy specimen, the CoCrAlY containing coatings debonded at or near the superalloy surface. These results suggested that the plasticity of the metallic constituent was in fact significant, and prompted the selection of nickel-chromium alloys as intermediate between nickel and CoCrAlY in both plasticity and resistance to sulfidation. Also, the pure ceramic overlayer was omitted, and the subsequent experiments were confined to studying the adherence of the graded composition layer.

#### COATINGS BASED ON NICKEL-CHROMIUM ALLOYS

Two nickel-chromium alloys were investigated as the metallic portion of the graded composition coatings. The equiatomic composition, designated as Ni50Cr, was selected primarily on the basis of its known sulfidation resistance. Nichrome, Ni20Cr, was chosen as a more plastic material while retaining a useful level of sulfidation resistance. Both materials were used in studies of the effect of composition profiles and oxygen partial pressure. Since their behavior was different only in degree from each other and that of pure nickel, the results will be discussed together. Generally, the Ni50Cr coatings were much less adherent, i.e. survived fewer thermal cycles, than the Ni20Cr coatings. This is believed due to the lower plasticity of the higher chromium alloy. It was also more difficult to obtain near-stoichiometric zirconia in coatings containing Ni50Cr, presumably due to the additional gettering action of the chromium. The results with Ni20Cr were not greatly different from those obtained with pure nickel.

Common to all three materials was an adverse effect on adherence as the coating microstructure was "improved". Improved is used here in the sense of fewer growth defects and a generally

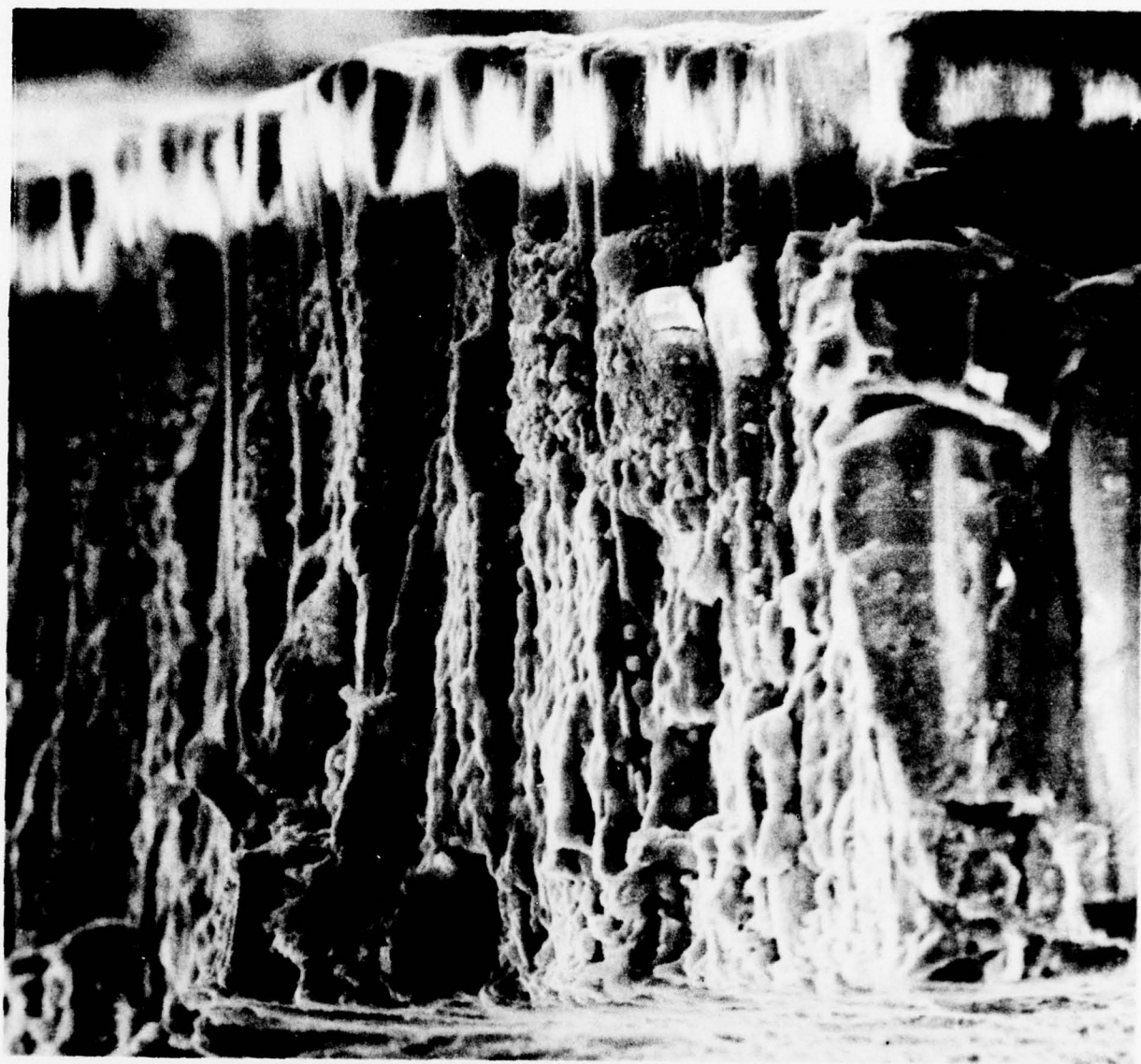


more coherent structure; compare Figure 2 and 3. This effect was attributed to the ability of the open structure to accommodate the tensile strain due to thermal mismatch simply by becoming more open, and thus avoid plastic deformation. The open structure approach was not pursued since the protective nature of such a coating is questionable.

#### EFFECT OF COMPOSITION PROFILE

The original intent was to first determine the behavior of an approximately linear composition-thickness profile and then explore the effects of increasing coating thickness to reduce the slope of the profile, and of employing non linear profiles. Since the sputtering rate is approximately linearly related to applied power, linear ramps of power vs time were used. However, since the cross contamination effects between the metal and ceramic targets were both greater in degree and more complex than anticipated, linear composition profiles were not produced. Typical power-time ramps and composition-thickness data are shown in Figure 4. The composition data have two features in common, a concave down curvature at the high metal end and a concave up curvature at the low metal end. The former is due to an undesired coverage of the ceramic target with metal sputtered from the metal target. This metal is resputtered when power is first applied to the ceramic target. The curvature at the low metal end is due to continued sputtering of metal at a low rate from the metal target during the period it is being covered by a ceramic film. The latter process was less effective in insulating the metal target and thus blocking sputtering than had been anticipated.

The variations in composition profile shown in Figure 4 were obtained by changing the initial dc power level and/or the rate of decrease; in one experiment the rate of increase of rf power was also varied. The effects of these variations



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FIGURE 3. Cross-Section of a Graded Nickel-Zirconia Coating Deposited Later in This Program. Note Finer, More Coherent Structure. SEM Photograph.

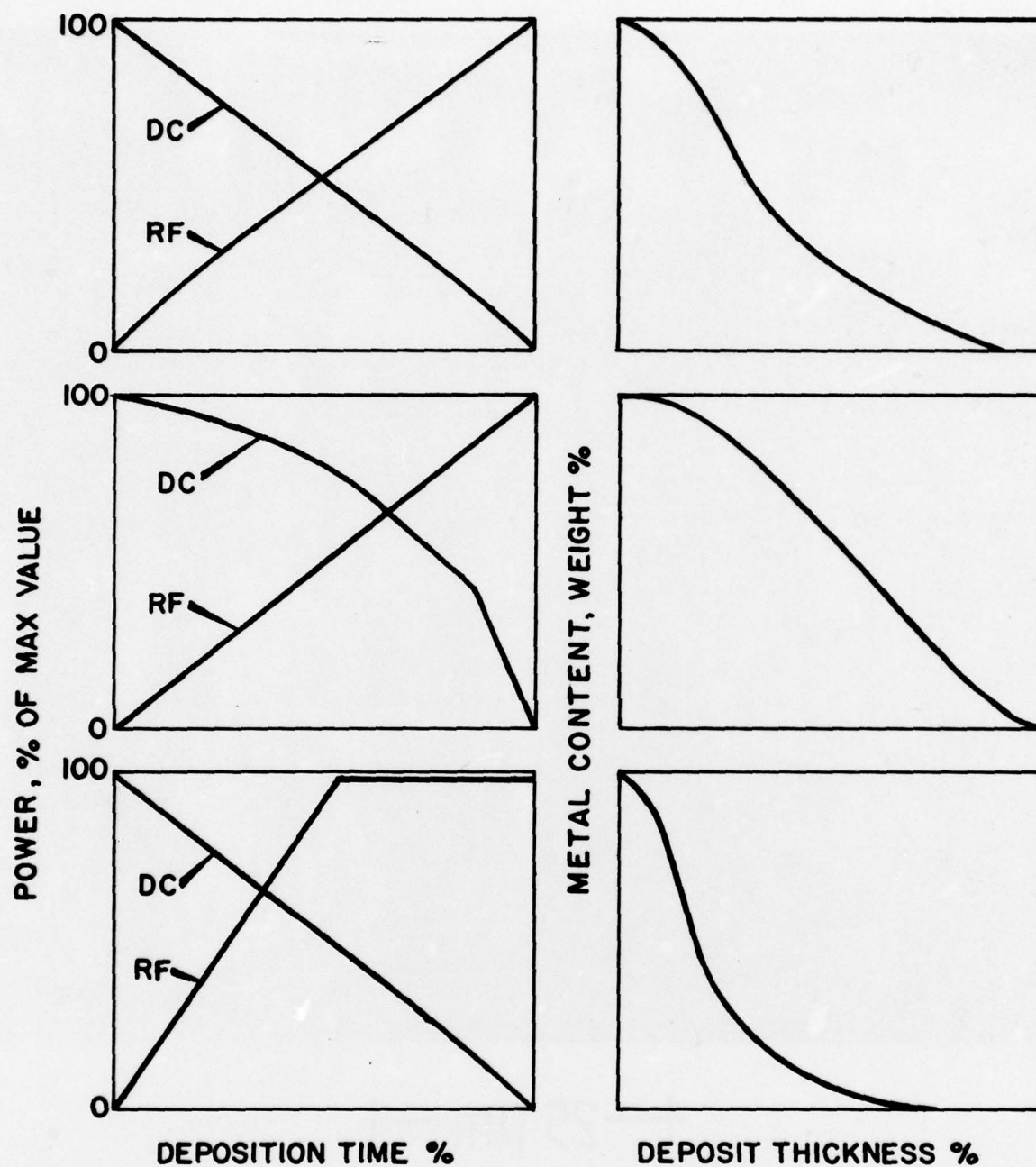


FIGURE 4. Schematic Representation of Power-Time Profiles, Left, and the Resulting Composition-Thickness Behavior.



on the composition profile were in the expected directions, but attempts to quantitatively predict composition profiles were not successful.

In general, the best correlation between the composition profile and coating adherence, as measured by the number of thermal cycles required to cause spalling, was given by the overall metal-ceramic ratio. As would be expected, adherence was directly related to this ratio. Within a group of coatings of similar thickness, adherence was improved by a decreased slope in the region where the ceramic was the major phase. However, increasing the coating thickness in order to decrease the slope of the entire profile did not improve adherence. A steep slope in the region of high metal content was not found to adversely affect adherence.

An attempt was made to correlate the location of failure interfaces in the thickness of the coating with the metal-ceramic composition and/or the slope of the composition profile at that point. No consistent pattern was observed.

The substrate superalloy had no discernible effect on coating adherence. Since the alloys investigated had similar elastic moduli, expansivities, and strength, no effect had been expected.

#### BURNER RIG TESTING

Several wedge specimens with coatings based on nickel-chromium alloys were tested in a burner rig at Annapolis.<sup>(5)</sup> The test consisted of two - 25 hour exposures to a 1700°F flame, using diesel fuel with 1% sulfur and air with 100 ppm salt. The specimens all exhibited spalling and net weight loss in spite of a weight addition from deposited salt. Since the magnitude of the latter is unknown, the actual coating loss cannot be determined. However, by assuming the salt deposition was constant for all specimens, the relative coating losses can be compared. The Ni20Cr coatings showed significantly smaller weight losses (10-15%) than the Ni50Cr coatings (35-65%). The difference was correlated with the depth of spalling as esti-



mated from photographs. Within the alloy groups, there were not sufficient samples to separate the effects of coating thickness and composition profile.

#### EFFECT OF OXYGEN PARTIAL PRESSURE

Sputter deposited oxide ceramics are generally sub-stoichiometric, i.e. deficient in oxygen, unless oxygen is added to the sputtering atmosphere<sup>(6)</sup>. The oxygen deficiency is greater when the deposition rate and/or substrate temperature is high. The latter effect is thought to be related to a decreased sticking coefficient for oxygen at increased temperatures<sup>(7)</sup>. In the present work, where both deposition rate and substrate temperature were high, the ceramic coatings were oxygen deficient even with oxygen added to the sputtering atmosphere. The deficiency was indicated by the dark color of the coatings, the presence of slight electrical conductivity, and in severe cases, spalling upon long exposures to air at elevated temperature. The spalling was attributed to the volume increase as the coating picked up oxygen from the air, since no spalling occurred in vacuum or during short exposure (minutes) in air.

Considerable difficulty was encountered in attempting to add sufficient oxygen to obtain stoichiometric ceramic coatings. Two features of the sputtering system account for this difficulty. First, the system is essentially a getter ion pump with a high pumping speed for active gases. Thus large amounts of oxygen may be bled into the system without observing a detectable partial pressure, e.g. by mass spectrometer. Secondly, the system tends to become unstable when a significant partial pressure of oxygen is obtained, e.g. in the range of 3 - 4%. Part of the instability is due to the getter ion pumping effect. Any momentary decrease in the discharge current reduces the pumping speed and thus increases the oxygen partial pressure. Since oxygen is less efficiently ionized than the inert gases,

the discharge current is further reduced, ultimately to zero. The discharge cannot be reignited until the oxygen pressure has been reduced by closing the inlet valve. An additional cause of instability is the increased tendency of the stray deposits collected on the various surfaces in the apparatus to flake and peel in the presence of oxygen. These flakes frequently cause electrical short circuits between electrodes and extinguish the discharge.

Various methods were explored to circumvent these difficulties. The most effective consisted of:

1. Introducing the oxygen immediately adjacent to the substrates rather than into the general chamber atmosphere.
2. Reducing the conductance between the sputtering chamber and the electron source compartment.
3. Reducing the discharge current as the amount of added oxygen was increased.
4. Altering the geometry of the apparatus surfaces which collect stray deposit to reduce the harmful effects of flaking.

Items (1) and (2) increased the effectiveness of the added oxygen, while item (3) permitted greater amounts to be added. Item (3) had a second effect in that both the deposition rate and substrate temperature were reduced, thus reducing the partial pressure of oxygen required. Item (4) reduced the probability of a deposition being prematurely terminated by flaking due to the added oxygen.

The modified power profile and oxygen addition profile is shown in Figure 5. With these profiles the outer skin of the coating consists of zirconia sufficiently close to stoichiometry that it does not spall due to a volume increase upon exposure

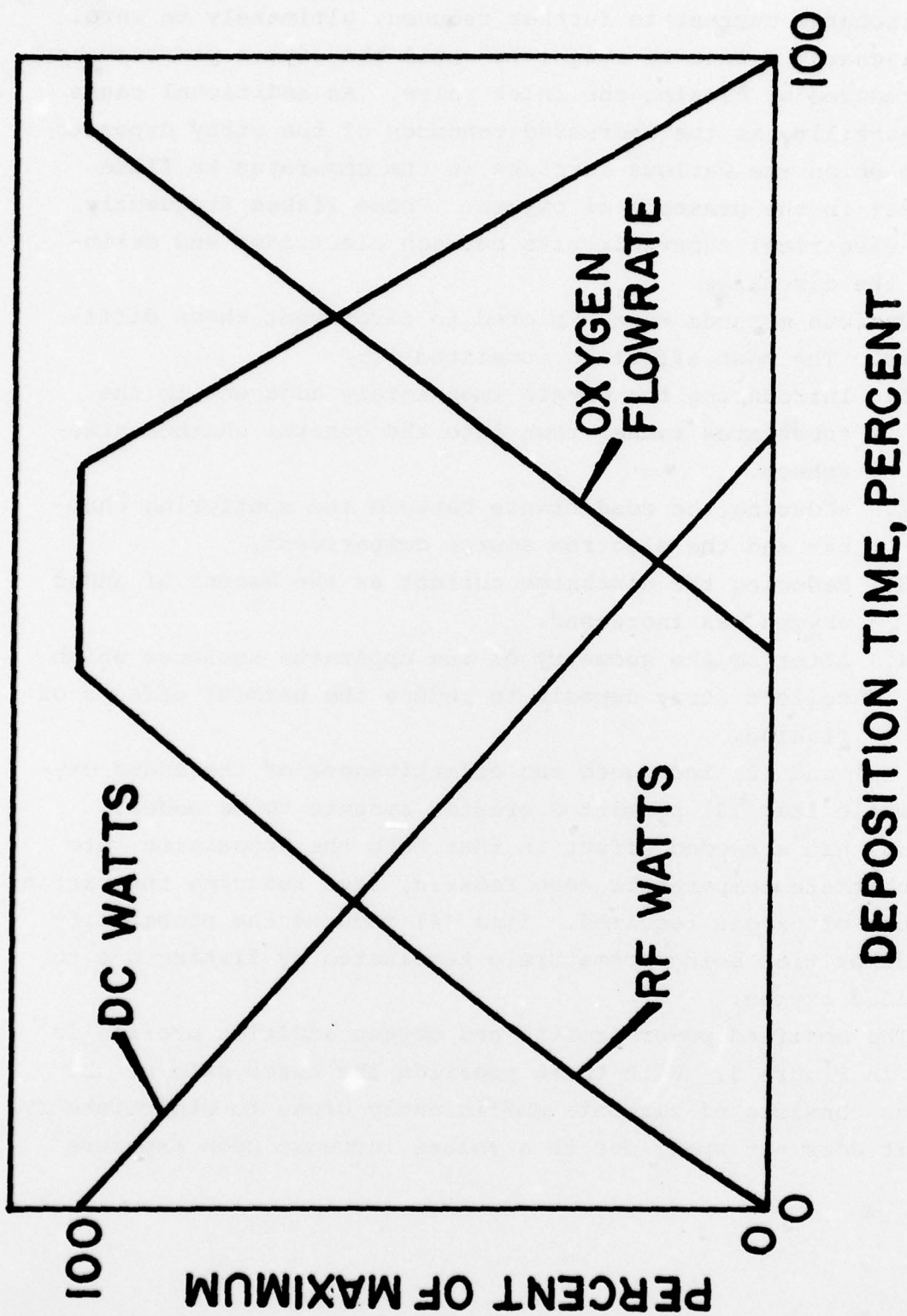


FIGURE 5. Modified Power Profile and Oxygen Flowrate Curve Adopted to Reduce the Oxygen Deficiency of the Zirconia Coatings.



to air at elevated temperatures. Although the ceramic material below this skin is still oxygen deficient, spalling is not observed for annealing times adequate to achieve saturation of the full coating depth.

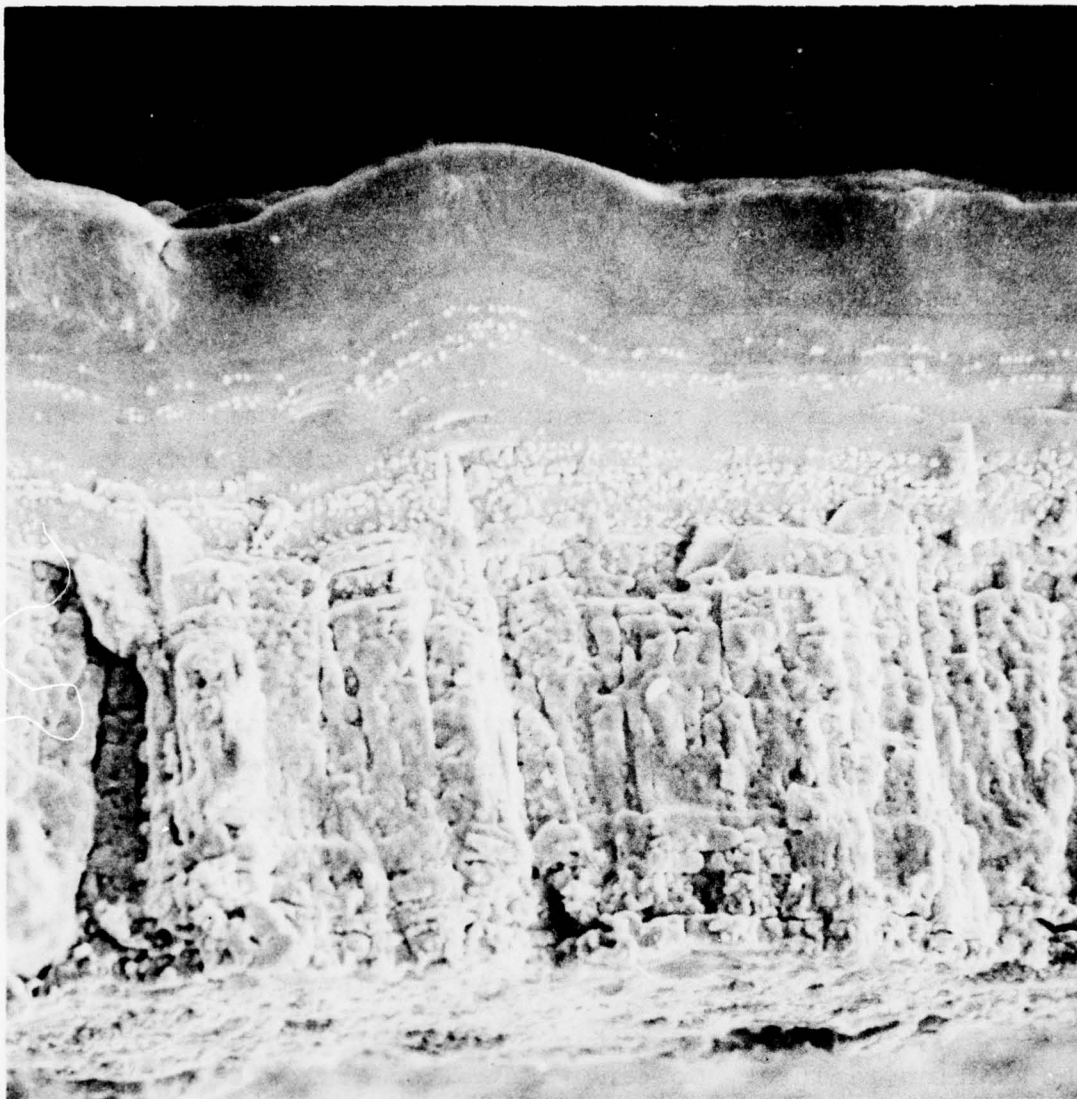
The changes made to achieve the closer approach to stoichiometry were not found to affect the adherence of the coatings in a significant way.

#### INVESTIGATION OF OTHER VARIABLES

##### Substrate Temperature

The bulk of the work reported here was performed with burner rig wedge and pin specimens. Because of the solid geometry of these specimens and the low thermal conductivity of superalloys, the substrate temperature was not controllable independently of the deposition rate. In a few experiments, however, hollow tensile specimens were employed with water and air cooling. Since only one such specimen could be used in each deposition, the results are insufficient to permit firm conclusions. However, the coatings deposited at low temperatures were somewhat more adherent, failed in a distinctly different manner, and were closer to stoichiometry than coatings deposited at the 600 to 700°C temperatures generally employed.

The grain structure of the low temperature deposits was significantly finer, as shown in Figure 6. The most significant difference however, was the lower apparent energy released in the coating failure. Coatings deposited at low temperature failed by gradual debonding of  $\sim 10 \text{ mm}^2$  areas, which remained partially attached to the substrate and each other as shown in Figure 7. In contrast, coatings deposited at high temperature failed audibly, and the debonded flakes, of  $\sim \text{mm}^2$  dimensions left the surface with an appreciable velocity. This difference is taken as an indication that low and intermediate substrate temperatures should be investigated further.



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FIGURE 6. Microstructure of a Graded Nickel-Zirconia Coating Deposited on a Water Cooled Substrate with the Power and Oxygen Profiles Shown in Figure 5. Note the Fine Grain Structure and the Featureless High Ceramic Region.



FIGURE 7. Comparison of Failure Behavior of Coatings Deposited on Cold (top) and 700°C (bottom) Superalloy Substrates.



### Substrate Bias Potential

A negative potential placed on the substrate is well known to modify the structure of sputtered deposits,<sup>(8)</sup> and may also affect the composition of multi-component systems.<sup>(9)</sup> The effects of a substrate bias potential are due to the ion bombardment of the growing deposit, which causes back-sputtering (which may be selective) and additional heat input. Alternately, grounding the substrate, which renders it positive with respect to the discharge, results in electron bombardment heating and perhaps surface desorption of gases. The intermediate situation is the isolation or floating potential, where the electron and ion currents cancel each other.

Since the coatings deposited in this work were electrically conductive up to the final stage of the graded composition layer, it was possible to investigate the effects of the three substrate potential conditions described above. No significant difference in adherence was observed, however, the surface roughness was less in the case of negative bias voltages, and the microstructure was finer grained. No difference was observed between the structures of deposits formed on grounded and floating substrates.

In future work, the system will be modified to permit placing an rf bias on the substrates, so that the effects on the ceramic microstructure and composition may be determined.

### Post Deposition Annealing

The effect of annealing coated specimens for several hours at temperatures of 750 to 950°C was consistently to improve coating adherence. The improvement was in both the number of thermal cycles to first failure and in a reduced areal fraction of spalling with further cycling. The reason for this effect is not clear. The possibility of stress relief being beneficial

seems unlikely since annealing would be expected to raise the stress-free temperature to the annealing temperature. This would increase the strain at the low temperature end of the thermal cycle where failure was observed.

The benefit of annealing may be related to the removal by diffusion of the discrete layer structure of the graded composition deposit. Since the layer structure, which arises from the rotation of the substrates between the opposed targets, was deliberately kept to small dimensions ( $< 50 \text{ \AA}$  thickness) and so was not resolvable by electron microscopy, this possibility could not be evaluated.

#### SUMMARY AND CONCLUSIONS

The application of zirconia and graded composition metal-zirconia coatings to superalloy specimens by high rate sputter deposition was investigated. The coatings were intended to improve sulfidation resistance and achieve a measure of thermal insulation of gas turbine hot section components. The objectives of the study were to determine the factors controlling adherence of the coatings and to find methods of accommodating the strain resulting from the large mismatch in thermal expansivity between zirconia and a typical superalloy, which amounts to  $6 \times 10^{-6}/^{\circ}\text{C}$ . The principal parameters found to govern the adherence of the coatings were the metallic constituent and its distribution profile in the graded composition layer. Pure zirconia, i.e. ungraded, overlayers were much less adherent than the graded composition layers. Within the group of metallic constituents investigated, adherence of the coatings correlated with the plasticity or ductility of the metals. Adherence improved in the direction; CoCrAlY, Ni50Cr, Ni20Cr, and pure nickel. The most important aspects of the composition profile

were the overall metal/ceramic ratio and the slope in the region where the zirconia was the major phase. High values of this ratio and shallow slopes were advantageous. Increasing the thickness of the graded composition layer in order to obtain a shallower overall slope did not improve adherence.

Improvements in the sputtering process which led to sounder, i.e. lesser defect density, coatings required higher metal/ceramic ratios to achieve similar adherence. The more open structures apparently offer greater accommodation for the thermal mismatch strain. The few results with deposits formed at low temperatures offer the hope that control of the initial stress state may offset this adverse effect of improved structure.

A second area of investigation involved means of overcoming the tendency of sputter deposited zirconia to be strongly oxygen deficient, particularly at the high deposition rates of interest for a production coating process. The oxygen deficiency of the coating was of concern primarily due to the spalling of the coating surface when exposed for long periods to high temperature air. The spalling was attributed to the volume increase upon oxygen pickup. Due to the limitations imposed by the sputtering system on the amount of oxygen which could be added during deposition, it was found necessary to combine a group of measures designed to increase the effectiveness of the added oxygen, reduce the amount of oxygen required, and increase the oxygen tolerance of the sputtering system. With these measures, it was possible to avoid this spalling phenomenon, although the deposited zirconia was still slightly deficient in oxygen.



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